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ANTIBACTERIAL AND PHOTOCATALYTIC ACTIVITYOF POMEGRANATE RIND EXTRACT DOPED TIO_2 NANOPARTICLES BY SOL-GEL METHOD

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ABSTRACT

Metal oxides exhibits extraordinary properties like hydrophobic nature and high energy band gap, hence it can be used in different types of applications such as in solar cell, photo catalysis, charge spreading devices, chemical sensors, microelectronics, electrochemistry, antibacterial products and textiles in the nano level due to their high surface to volume ratio. Generally various synthesis techniques are available to prepare TiO_2nanoparticles. In this present paper synthesis of TiO_2nanoparticles were focused using Green synthesis using pomegranate rind extract as one of precursor. Pure TiO_2 exhibits low photocatalytic property due to rapid recombination of photo-activated electrons and holes. Extract of Pomegranate Rind (PRE) was considered to dope into TiO_2photocatalyst in order to enhance the photocatalytic property and bacterial inactivation efficiency. The PRE doped TiO_2 nanoparticles were prepared by sol-gel method and calcined at 400°C for 2h. The synthesized powders were characterized by Uv-Vis, XRD, SEM, FT-IR. Photocatalytic activity and bacteria killing effect was determined by means of degradation of methyl orange solution and inactivation of E.Coli bacteria. PRE doped TiO_2 has an effect on inhibition of anatase crystal growth, led to the enlargement of the composite specific surface area exhibits highest photocatalytic activity and E.Coli inactivation efficiency.

INTRODUCTION

The widespread use of antibiotics and the emergence of more resistant and virulent strains of micro-organisms (Russel 2004; Kun *et al.,*2006; Aiello *et al.,* 2009) have caused an urgent need to develop alternative sterilization technologies. Using the superb photocatalytic effect of titanium dioxide (TiO_2) is a conceptually feasible technology for this material is easy and inexpensive to produce in industrial scale. Photocatalytic TiO_2 samples have been shown to eliminate organic compounds and to function as disinfectants (Maness *et al.,*1999). Traditional TiO_2 photocatalyst, however, is effective only upon irradiation of UV-light at levels that would also include serious damage to human cells. This greatly restricts the potential application of TiO_2 for use in our living environments. Recently metal-ion doped or Herbal and Fruit extract doped anatase based TiO_2photocatalysts have been identified to be active upon visible-light illumination (Iwasaki *et al.,* 2000; Asahi*et al.,* 2001) offering the possibility to overcome this problem. It is believed that nanometer-sized Anatase phase particles have large surface area are efficient for the decomposition of pollutants in air and water (Ohno *et al.,*2001). Further, more it is also found that the presence of Anatase phase is important in some of the photocatalytic reactions where oxygen is used as electron acceptor (Sugimoto *et al.,* 2003). The antibacterial activity of visible light responsive photocatalysts has been reported by several groups (Li *et al.,* 2007; Yu *et al.,* 2003; McDonell *et al.,* 1999). Since photocatalyst based anti-microbial technologies are still under development. In this study, the effect of Pomegranate Rind Extract doped in TiO_2photocatalyst on TiO_2, crystallite size, Surface Morphology, FT-IR, photocatalytic reaction and antimicrobial activity were tested.

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MATERIALS AND METHODS

Titanium (IV) isopropoxide (TTIP), Pomegranate Rind Extract (PRE), were used as starting materials and ethanol was used as solvent. The TiO_2 doped PRE powders were prepared through a conventional sol-gel method (Fig.1). Firstly, Pomegranate Rind were dried, crushed, powdered and stirred for 30 minutes in ethanol. The filtered ethanolic extract of Pomegranate Rind mixed with TTIP for 1h. at room temperature and followed by adding droplets of 4M NH_3 into the solution until pH about 3-4 (Hasan *et al.,*2008). Finally, the solution was dried at 100°C for 24 h. and calcined at the temperature 400°C for 2h. The synthesized powder was ground and submitted to determine the particle size. The crystallinity of PRE - TiO_2 powder was determined by X-ray diffraction (XRD) analysis using X-ray diffractometer (model –D500 siemens) with CuKα radiation. The surface morphology was observed using scanning electron microscopy (SEM JSM 6400 JEOL). Spectroscopic analysis was performed by using Uv-Vis spectrophotometer. The hydroxyl content of the sample was investigated by FT-IR analysis spectrometer. The antibacterial activity was studied by colony forming units per milliliter, after incubation.

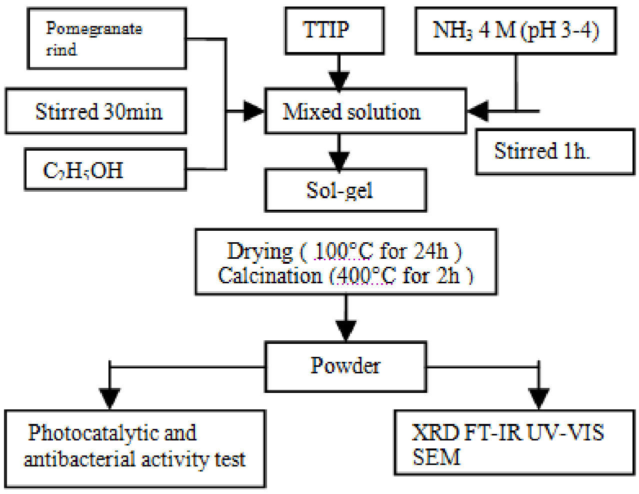

Fig.1. Preparation of TiO_2 doped PRE by sol-gel method

Photocatalytic reaction test

Photo-degradation of organic compounds using PRE-TiO_2 as catalysts occurs when catalyst isilluminated with sunlight in presence of water containingdissolved oxygen and organic contaminants (Zep *et al.,*1992; Kokila *et al.,* 2011). The organic contaminants are decomposed to CO_2 and H_2O under these conditions

PRE-TiO2 + hν —> e^-_{cb} +h^+_{vb}
h^+_{vb} +OH^- —> • OH
h^+_{vb} +H_2O —> • OH +H^+
e^-_{cb} + O_2 —> $O_2^{\bullet -}$ (superoxide ion)
IGOR + $OH^\bullet$—> Co_2 + H_2O +HNO_3

Where, h^+ represents the hole with positive charge generated at the surface of catalyst. The methyl orange is attacked by hydroxyl radicals formed as given in the above equation and generates organic radicals or other intermediates. Finally the parent compounds and intermediates are oxidized into CO_2, SO_2^{2-}, NO_3^- and H_2O.

The photocatalytic activity was evaluated by the degradation of methyl orange under UV-Visible spectrophotometer irradiation using four 50 W black light lamps. A 400 ml methyl orange with a concentration of $1x10^{-5}$M was mixed with 1.5g of photocatalytic powder (pure TiO_2, and TiO_2 doped with PRE) under UV irradiation for 0,15,30,45,60,75 and 90 min. After photo-treatment for a certain time the concentration of treated solution was measured by ultraviolet visible spectrophotometer (UV-Vis).

The percentage of degradation of methyl orange is calculated by:

$= 100 (C_O\text{-}C)/ C_O$

Where,
C_O→ the concentration of methyl orange aqueous solution at beginning ($1X\ 10^{-5}$M)
C → the concentration of methyl orange aqueous solution after exposure

RESULTS AND DISCUSSION

Fig.2. shows the UV-Visible spectra of pure and PRE doped TiO_2. Using PRE as dopant has increased TiO_2's photocatalytic activity due to the shift in optical absorption, also known as the red shift.

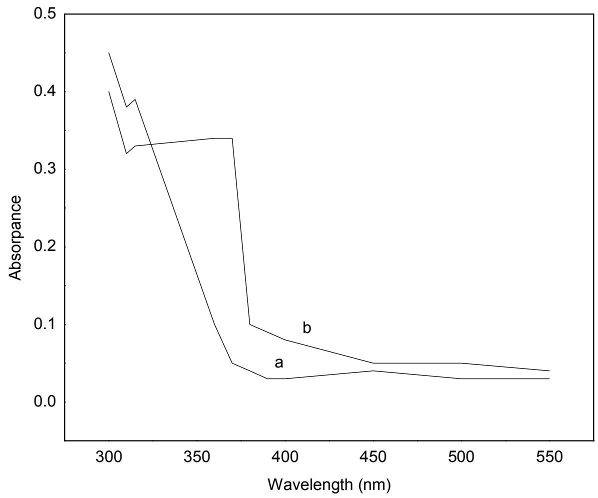

Fig. 2. UV-Vis Absorption spectra of a) pure and b) PRE doped TiO_2 powder

The absorption of pure TiO_2 sample is at around 370 nm; the dopant not only shifts the absorption edge towards the visible region but also increases the absorption of TiO_2 in whole visible range (longer wavelength 400-800 nm), causing the shift. Particle size of pure TiO_2 and PRE doped TiO_2 powder after calcinations at 400° C for 2h and ground by using mortar were calculated using the Scherrer's formula (Cullity and Stock 2001) from the full width at half maximum [FWHM]

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of the X- ray used, β is the [FWHM] and θ is the angle between the incident and the scattered X-ray. From Fig.3 all samples have shown similar peaks with the highest peak at 24.35° which was indicated as (101) plane 100% anatase phase and the peak at 33.3° (104) plane shows the presence of PRE content. The crystallite size of pure and PRE TiO_2 were 9.166 and 8.045 nm respectively (Zhang *et al.,* 1998). The FT-IR spectra of the TiO_2 doped with PRE Fig.4 shows the increase in intensity of peak, the broad bands at 2350 - 3500cm^{-1} are assigned to O-H for absorbed water molecules and Ti-OH (Zhou *et al.,* 2006). This suggests that the hydroxyl content increases with respect to the dopant into the sol (Cromer *et al.,* 1955; Wong *et al.,* 2006). SEM image of PRE-TiO_2 Fig.5 shows that the agglomeration of synthesized composite powders was observed (Kim *et al.,* 2000).

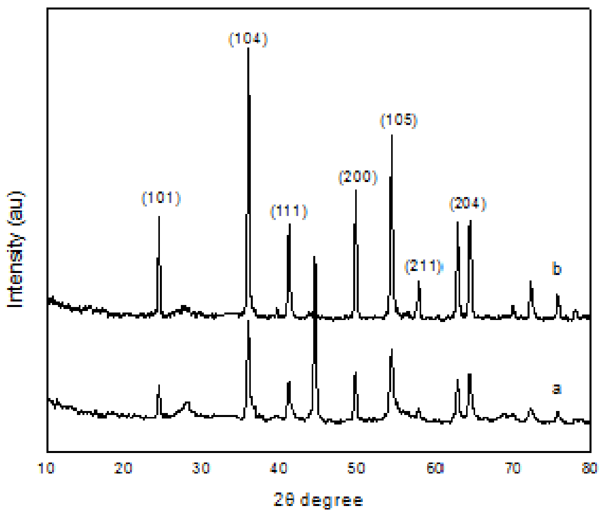

Fig. 3. XRD patterns of a) pure b) PRE-doped TiO_2 powders annealed at 400°C

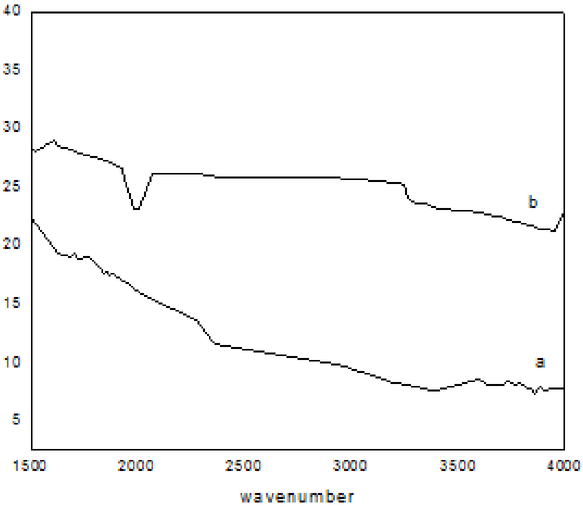

Fig. 4. FTIR spectra of a) PRE doped TiO_2 and b) pure TiO_2 samples

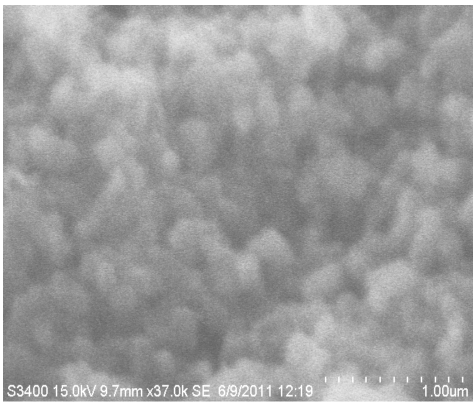

Fig. 5. SEM image of PRE-doped TiO_2 powder annealed at 400°C

Photocatalytic activity

The ethanolic Extract of Pomegranate was used as dopants is able to enhance the attachments of the functionalized organic pollutants to the doping ion active sites (Zhou *et al.,* 2006). Fig.6 shows the degradation of methyl orange solution using PRE-doped TiO_2 powders, pure TiO_2 and doped TiO_2 powders under UV light for15 min until 90 min (Yu *et al.,* 2001). The degradation effect of methyl orange by PRE-doped TiO_2 was better than those of pure TiO_2 (Sarmah *et al.,* 2011; Sonawane *et al.,* 2004; Erkan *et al.,* 2006).

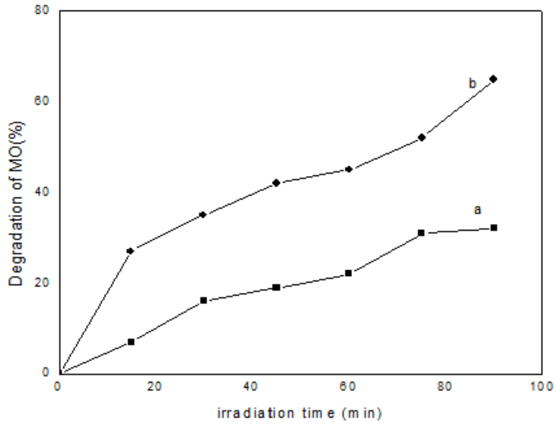

Fig. 6. Degradation of methyl orange solution for a) pure TiO_2 and b) PRE-TiO_2

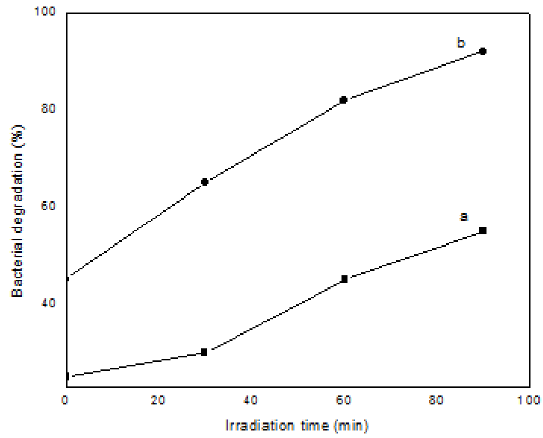

Fig. 7. Antibacterial efficiency of Escherichia coli bacteria of a) pure TiO_2 and b) PRE-TiO_2

After 90 min of testing, the percentage degradation was 32% (pureTiO_2) and 65% (PRE-TiO_2). This increase in photocatalytic activity with PRE doping is related to shift in optical absorption of the catalyst in visible region. TiO_2 absorbs only UV energy (below 400nm) whereas doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The presence of metal ions on the surface of the photo catalyst particles improves the rate of electron transfer to O_2 and consequently has a beneficial effect on the photo- oxidation rate of organic species (Li *et al.,* 2008). The more number of pores increases the hydroxyl content. In heterogeneous photo catalysis, the illumination of semiconductor produces electrons (e^-) and holes (h^+). The holes (h^+) are combining with OH^- ions and there is formation of hydroxyl radicals (h^+_{vb}+OH^- —> • OH). These surface hydroxyl radicals formed on the surface of the photo-catalyst are oxidizing species which ultimately affects the photo-catalytic activity. This suggests that the increase in hydroxyl content of the film increases the photo-catalytic activity. Also stated that these dopant exists only as the recombination centre for the electron /holes, thus having no noticeable effect on the reaction rate.

Antibacterial activity

The study of antibacterial activity of titanium dioxide nanoparticles for Escherechia Coli, gram negative bacteria is shown in Fig.7. The bacterial degradation efficiency is high for Pomegranate rind doped TiO_2 than the pure TiO_2, is evident from the zone of inhibition (Balashanmugam *et al.,* 2013; Leenders *et al.,* 2013). It shows that TiO_2 nanoparticles inhibits the growth of microorganisms and thus used in waste water treatment.

Conclusions

It was apparent that Pomegranate Rind doping has an effect on hindrance of anatase crystal growth; therefore the crystallite sizes of TiO_2/PRE nanoparticles 8.045 nm are smaller than those of pure TiO_2 9.166 nm. This leads to enhancement of photocatalytic activity and disinfection efficiency due to their large surface area. The surface hydroxyl content increases the photocatalytic activity of the photo-catalyst. TiO_2/PRE nanomaterials have strong antimicrobial properties through a mechanism including photocatalytic production of reactive oxygen species that damage cell components and viruses, its potential to be activated by visible light or sunlight. Therefore these composite TiO_2 nanoparticles will be utilized for fresh food packaging films.

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